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DETAILED MINERALOGICAL EXAMINATION OF ALTERATION PRODUCTS IN CORE WA20 FROM WAITE AMULET TAILINGS

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MICROMEDIA

DETAILED MINERALOGICAL EXAMINATION OF ALTERATION PRODUCTS IN CORE WA20
FROM WAITE AMULET TAILINGS

by

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ABSTRACT

Alteration of the Waite Amulet tailings has resulted in the formation of (1) a strongly oxidized upper zone largely depleted of sulphides; (2) an intermediate zone wherein pyrrhotite, which is the sulphide most susceptible to alteration, has been replaced extensively; (3) a bottom zone in which pyrrhotite is largely intact. Pyrrhotite in the oxidized zone has been replaced mainly by goethite, but in the intermediate zone the alteration products are goethite, native sulphur, marcasite, and iron sulphates that are probably of the type $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. Other alteration minerals are bassanite, gypsum, lepidocrocite, and jarosite.

ÉTUDE MINÉRALOGIQUE DÉTAILLÉE DES PRODUITS DE DÉFORMATION DE
LA CAROTTE WA20 PROVENANT DES RÉSIDUS DE WAITE AMULET

par

J.L. Jambor

RÉSUMÉ

La déformation des résidus de Waite Amulet a mené à la formation (1) d'une zone supérieure fortement oxydée et considérablement démunie de sulfures; (2) d'une zone intermédiaire dans laquelle la pyrrhotite, un sulfure plus susceptible à se déformer, a été largement remplacée; (3) d'une zone de fond dans laquelle la pyrrhotite est demeurée considérablement intacte. La pyrrhotite de la zone oxydée a été remplacée principalement par de la goethite, mais dans la zone intermédiaire les produits de déformation sont la goethite, le soufre natif, la marcasite et les sulfates ferreux qui sont probablement du type $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. Enfin, parmi les autres minéraux de déformation, on trouve de la bassanite, du gypse, de la lépidocrocite et de la jarosite.

INTRODUCTION

The Waite Amulet minesite is about 20 km north of Noranda, Quebec. The original mill at the mine was constructed in 1929, and feed from ten separate orebodies in the area was eventually passed through the mill prior to its closure in 1962. Siwik (1986) reports that the operations resulted in 5.9 million tonnes of sulphide-rich tailings, 2 to 15 m thick, that are in an elevated 41 hectare dam. The tailings and site are undergoing detailed hydrogeochemical studies as part of the national RATS (Reactive Acid Tailings Study) program. In this specific case Noranda Research Centre and CANMET are joint participants in the study.

As part of the Waite Amulet investigation, nine holes were cored through the tailings pile in 1985. Core samples from hole WA20 were examined mineralogically by Petruk and Pinard (1986), and their image analysis study provided quantitative abundances of the tailings minerals and alteration products that occur in one vertical section through the tailings pile. The alteration products are complex and extremely fine-grained mixtures that are difficult to identify as specific mineral phases. The main objective of the present study was to investigate in more detail the mineralogical character of the alteration products to see whether they are largely amorphous or crystalline, and to identify the crystalline phases.

SAMPLES AND STUDY METHODS

Ten tailings samples (WA20-1 to WA20-10) were available. These had been screened into +37 micrometre (+400 mesh) and -37 micrometre fractions, and bottled separately. As well, the 20 polished sections used by Petruk and Pinard (1986) in their study of these screened fractions were available.

Only the coarser (+37 micrometre) fractions were used in the present investigation. A cursory examination of the ten polished sections showed that there was considerable mineral variation from sample to sample, as is evident in the image analysis results obtained by Petruk and Pinard (see Table 1). Consequently, a portion of the tailings was removed from each of the 10 bottles of +37 micrometre sample, and each was separated into three fractions according to the reaction to a hand magnet. The fractions were examined megascopically (Table 2) and under a binocular microscope, and aggregated material (clumps) was selected for an additional nine polished sections. Eventually about forty Debye-Scherrer X-ray patterns were obtained from material selected under the metallographic or binocular microscopes, and a few supplementary energy dispersion and wavelength microprobe analyses were used to confirm the X-ray diffraction and microscopic observations.

RESULTS

Hand-magnet separations

Table 2 summarizes the megascopic observations resulting from the magnetic separation of the +37 micrometre samples. In all samples the colour of the magnetic fraction is darker than that of the non-magnetic fraction because magnetite and pyrrhotite report to the magnetic portion whereas the light-coloured silicates are left behind. As shown in Table 2, both the magnetic and non-magnetic fractions of all samples except WA20-6 show progressive colour darkening with increasing depth. The reversal for WA20-6 probably reflects its relatively high goethite content combined with a low content of magnetite plus total sulphides (Table 1).

The hand-magnet separations resulted in a pronounced size grading in that nearly all of the coarse material was removed from the non-magnetic fraction and reported in variable proportions to both of the magnetic fractions, though predominantly to the more magnetic one. This coarse material consists of weakly to moderately cohesive aggregates that form clumps up to 5 mm in diameter, though most are 2 mm or less. These larger clumps contain the same mineral species that are present in the associated non-aggregated and minutely aggregated fractions, but some clumps show clearly that layering is present (Fig. 1). The layering is evident mainly because of variations in the proportions of minerals such as pyrite, pyrrhotite, and magnetite. Differences in grain sizes are less conspicuous, but a few examples have been observed (Fig. 2,3). These observations, together with the data of Petruk and Pinard (Table 1), fit well with the assumption that substantial changes in mineral proportions occurred during the many years of tailings deposition. Post-depositional, in situ alteration is only of secondary importance in accounting for major mineral variations in all samples except those nearest the surface.

Alteration minerals

Bassanite, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, occurs in small amounts throughout the tailings cross-section. Under a binocular microscope the mineral can be seen as snow-white partial coatings on some grains, and as an interstitial binder among grain aggregates. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was identified in only one X-ray diffraction pattern and is present with admixed bassanite. Anhydrite, $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, has not been detected.

Bassanite is unstable when exposed to water, and thus is lost readily in the routine preparation of polished sections. Dissolution of bassanite accounts for its absence in the image-analysis sections, and similarly accounts for the excessive pitting observed in some of the clumps mounted in sections.

Jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, occurs mainly in the near-surface oxidized zone. X-ray powder patterns show that the mineral deviates from its end-member composition, but energy dispersion analyses of the X-ray mounts indicate that substantial amounts of potassium are present. The mineral is, therefore, probably normal K-jarosite in which hydronium and sodium have substituted for part of the potassium.

A clear coating on part of a tailings clump from sample WA20-7 (2.1 m) proved to be a mixture of melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and ferrohexahydrate, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$. Melanterite is unstable and readily loses part of its water to form lower hydrates, especially the tetrahydrate. Minerals of this type also are readily soluble in water and reprecipitate on drying. Thus there is a strong possibility that the above sulphate minerals are not in their original hydration states. As is discussed in the next section, however, water-soluble iron sulphates are present in the tailings.

The main alteration product in most of the tailings is goethite, $\text{FeO}(\text{OH})$. In the tailings samples the mineral is always heterogeneous when viewed under the microscope, and thus no area was selected for microprobe analysis. Despite this optical heterogeneity, a few of the X-ray powder-diffraction patterns of the mineral gave normal cell dimensions and a diffraction-line sharpness indicative of good crystallinity. Other X-ray patterns gave poor patterns identifiable as goethite, but it is not certain

whether the inferior quality arises from poor crystallinity or inadequate X-ray material, or perhaps both. Lepidocrocite, $\text{FeO}(\text{OH})$, was detected in only two X-ray patterns. In contrast to goethite, lepidocrocite appears to be poorly crystalline and the identification, although fairly certain, is not absolute.

Native sulphur was identified in several X-ray powder patterns. The mineral was detected as an interstitial binder in the tailings clumps, but is more widespread as a component of the alteration rims around pyrrhotite. Despite the X-ray diffraction evidence of the presence of sulphur in the rims, the mineral could not be found as a discrete phase when these rims were examined under the scanning electron microscope. Energy dispersion analyses show that the alteration cores and rims have variable proportions of Fe and S, exactly as has been reported by Petruk and Pinard (1986). The X-ray diffraction evidence indicates that the alteration areas that are grey in reflected light consist of mixtures of iron oxide (mainly goethite) and sulphur. Despite this evidence, the additional presence of iron sulphate can be inferred from the microprobe results that are discussed below.

The alteration of pyrrhotite to extremely fine-grained intergrowths of pyrite and marcasite, both FeS_2 , is well known and commonly takes the form of "bird's-eye" textures and minute veinlets. Altered pyrrhotite having this type of texture and mineralogy was observed only rarely in the tailings grains. Instead, the typical texture is to have marcasite formed at the margins of atoll-texture pseudomorphs after pyrrhotite (Fig. 3)

Microprobe analyses of three atoll-texture grains are given in Table 3. In reflected light the marcasite rims do not have the brightness of typical marcasite, and this lower reflectance suggests the possible presence of sub-

microscopic intergrowths with a non-sulphide phase or phases. This inference is supported by the low analytical totals, and also is supported by the observed gradation to duller, less metallic-looking rims. A similar gradation seems to extend to phases that are completely non-metallic in appearance.

Although X-ray patterns gave only goethite and sulphur as the identifiable non-sulphide components formed by pyrrhotite alteration, the additional presence of iron sulphate is indicated by microprobe analyses at wavelengths that discriminate "sulphate-type" versus "sulphide-type" sulphur. Table 3 gives the microprobe results obtained from dark, non-metallic cores associated with marcasite as shown in Figure 4. The analyses correspond roughly with a formula of $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ where n is less than 2. Compounds of this type, however, are not stable in vacuum or under the electron beam; this susceptibility to dehydration was mentioned previously in the description of ferrohexahydrite.

The analytical results, combined with the known presence of ferrous sulphates in the tailings not mounted in polished sections, suggest that the components in the alteration rims and pseudomorphs are mixtures that consist predominantly of goethite, sulphur, and $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. The amount of ferrous sulphate is difficult to estimate from the polished sections because polishing normally involves contact with water, and thus there is an attendant loss of soluble sulphates. This type of loss probably accounts for the severe pitting noted to accompany the altered pyrrhotite in the polished sections. The polished section containing the analyzed iron sulphates (Table 3) was prepared using a non-aqueous medium. Addition of a drop of water to the polished surface rapidly led to severe pitting and the subsequent precipitation of abundant crystals of melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Alteration trends

The colour variations (Table 2) show that, with one exception, there is a progressive downward darkening of the tailings. This colour variation coincides well with the microscopic observations of alteration intensity: the rust-brown upper samples represent a zone of strong oxidation, and the medium-brown samples represent an intermediate zone of moderate alteration that is gradational to a bottom zone of weak sulphide alteration.

The uppermost two samples at 0.3 m and 0.6 m evidently differed substantially in their original sulphide contents. Remnants of pyrrhotite were not seen in either sample, but only the near-surface one shows abundant outlines characteristic of pseudomorphs after pyrrhotite and pyrite. The few sulphide grains observed in the near-surface sample occur predominantly as small inclusions (≤ 6 micrometres) protected by enclosure in silicates and magnetite; sulphides in the deeper sample are more abundant (Table 1) and are more common as free grains. In both samples goethite is abundant and, judging from the X-ray diffraction results, jarosite is concentrated in this zone. Goethite in the upper sample partly to completely rims all magnetite grains, generally as irregular and heterogeneous rinds that are only 1 to 2 micrometres wide, though widths of 5 to 10 micrometres are locally present. The majority of silicate grains also have goethite rims. Weaker alteration of the deeper sample at 0.6 m is indicated by its higher sulphide content and the presence of fewer goethite rims on magnetite. As well, goethite rims on silicates are less well developed in thickness and uniformity, and some silicate grains are free or almost free of rims.

The next deeper sample at 0.9 m differs significantly from those in the near-surface, strongly oxidized zone. The relative stability of magnetite is evident from its persistence and weak alteration in the strongly oxidized

zone; nevertheless, the sample at 0.9 m contains substantially less magnetite (Table 1) even though alteration is much weaker. This change is considered to reflect a variation in the components of the primary feed (i.e., original, unaltered tailings). The sample at 0.9 m contains abundant sulphides (Table 1), with pyrite predominating, and this depth marks the first appearance of numerous remnants of pyrrhotite. Iron oxide rims on silicates are almost absent, and alteration is largely confined to extensive replacement or complete pseudomorphism of the pyrrhotite. Minerals identified in the alteration rims are goethite, native sulphur, and lepidocrocite.

The next deeper group of samples at 1.2, 1.5 and 1.8 m has similarities in that both pyrrhotite and total sulphide contents are relatively high, and goethite rims on silicates are common. Goethite rims on magnetite are noticeably more pronounced in the sample from 1.5 m. The main indication of sulphide alteration is the partial replacement of pyrrhotite by rims containing mixtures of sulphur and goethite. The deepest sample (1.8 m) also marks the approximate depth at which secondary marcasite appears as a readily recognized component of some of the rims on pyrrhotite. Petruk and Pinard (1986) detected jarosite in the sample from 1.8 m, and marcasite in the sample from 1.5 m.

The next deeper sample, at 2.1 m, shows a very large increase in original sulphides, especially pyrite, and a readily observed decrease in the intensity of alteration. Goethite rims on silicates are extremely thin and occur sparingly, but the most distinctive indication of decreased alteration is that many pyrrhotite grains have only narrow alteration rims, and on many other grains these rims are incomplete. The adjacent, deeper

sample (WA20-8) is similar except that it shows both a slight but perceptible increase in goethite rims on silicates, and a decrease in the amount of marcasite in the rims around pyrrhotite.

The last two samples at the bottom of the tailings pile show the least amount of sulphide alteration. Pyrrhotite is abundant in both samples, and many grain edges are unaltered. Goethite is sparse and is largely confined to pyrrhotite replacement. These two samples show the best development of marcasite rinds on pyrrhotite.

Table 4 summarizes the alteration trends. Because of the difficulties in visually observing native sulphur, chemical analyses for elemental sulphur were obtained for four samples; the results (Table 4) show that sulphur is relatively low both in the strongly oxidized zone and in the least-altered bottom samples, but is present in substantial amounts in the intermediate alteration zone. These results fit well with the mineralogical data. Judging from the mineralogical observations it was anticipated that soluble iron sulphate would be highest in the intermediate zone and lowest in the strongly oxidized upper zone. The results obtained from five samples leached with water at room temperature are given in Table 5. Additional chemical analyses would be necessary to distinguish the contributions made by soluble calcium sulphate versus soluble iron sulphate; at this point it is only speculation that the high SO_4 value for sample WA20-2 (0.6 m) represents high calcium sulphate, whereas the rise in SO_4 values in the intermediate zone reflects increased iron sulphate.

CONCLUSIONS

1. Core WA20 through the Waite Amulet tailings shows substantial variations in the proportions of minerals that were discharged to the tailings. Despite these variations, which are quantitatively evident in the data of Petruk and Pinard (1986), there is good species uniformity in that pyrite plus pyrrhotite account for >95% of the original sulphides throughout the core.
2. Bassanite, $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, occurs throughout the core. Large amounts of agricultural limestone were added to neutralize the tailings surface, and this provides a ready source of calcium to react with acidic sulphate solutions generated from the decomposition of sulphides.
3. Alteration of the tailings can be divided into three general zones: (1) a strongly oxidized near-surface zone depleted in sulphides; (2) an intermediate zone in which pyrrhotite, the sulphide least immune to alteration, has been strongly attacked but not obliterated; (3) a bottom zone of weak alteration in which pyrrhotite is largely preserved and alteration rims vary from narrow, to incomplete, to absent.
4. The principal alteration minerals are goethite, sulphur, and ferrous sulphates probably of the type $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. Other minerals identified are jarosite, lepidocrocite, and marcasite. Sulphur is abundant in the intermediate zone, and marcasite is most evident near the lowest part of the intermediate zone.
5. Polished sections of the tailings should be prepared using non-aqueous media in order to minimize losses of water-soluble phases.

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- Siwik, R.S. (1986): Hydrogeochemical investigation of reactive tailings at the Waite Amulet tailings site, Noranda, Quebec - 1985 program. Contract Report OSQ85-00101.

Figure 1. Tailings aggregate from the magnetic fraction of sample WA20-4 (1.2 m) showing a silicate-rich layer (dark, at top) overlying a layer rich in magnetite (m, medium grey) and sulphides (white). Lined white grains are partly altered pyrrhotite; unaltered white grains are pyrite. Some of the silicate grains are enclosed in thin rims of iron oxide. Reflected light, air; scale represents 0.25 mm.

Figure 2. Coarse silicates with sparse pyrite (py) and magnetite (m) in an aggregate from sample WA20-9 (2.7 m). Note contrast in grain size as compared with Figure 3.

Figure 3. Magnetite-rich aggregate from WA20-9, photographed at the same magnification as Figure 2, showing extensive alteration of pyrrhotite to atoll-texture pseudomorphs in which the white rims are marcasite. Reflected light, air; scale represent 0.25 mm.

Figure 4. SEM photograph showing pyrrhotite altered to marcasite rims and iron sulphate cores. Microprobe analyses for grains 2 and 3 are given in Table 3.

Table 1. Image analysis data for +37 m fractions from core WA20*

Sample depth (metres)	WA20-1 0.3	WA20-2 0.6	WA20-3 0.9	WA20-4 1.2	WA20-5 1.5	WA20-6 1.8	WA20-7 2.1	WA20-8 2.4	WA20-9 2.7	WA20-10 3.0
Total										
silicates ¹	38.5	51.2	76.4	66.5	22.0	63.6	21.5	40.1	39.7	11.3
Magnetite ²	46.8	43.6	10.4	13.5	37.9	7.5	12.7	19.4	18.6	7.5
Sulphides ³	0.4	3.9	7.7	9.9	22.0	14.3	57.2	29.1	35.8	77.7
Goethite	14.2	1.4	5.1	8.1	5.8	7.3	2.8	6.3	3.1	1.1
Altered										
pyrrhotite	0.0	0.1	0.4	2.0	12.2	7.3	5.8	5.1	2.9	2.4
Magnetite + sulphides	47.2	47.5	18.1	23.4	59.9	21.8	69.9	48.5	54.4	85.2

*Condensed from Table 3 of Petruk and Pinard (1986). Quantities are in wt. %.

1. Quartz, K-feldspar, chlorite, amphibole and pyroxene
2. Reported as magnetite/hematite
3. Pyrite and pyrrhotite mainly
Pyrrhotite > pyrite; all others have pyrite > pyrrhotite

Table 2. Colour variations of the hand-magnet separates of the +37 m fractions

Sample number	Depth, metres	A (non-magnetic fraction)	C* (strongly magnetic)	Colour group
WA20-1	0.3	rust-brown, lightest of all samples	darker; sparse in clumps	1
WA20-2	0.6	similar to 1A	similar to 1C	1
WA20-3	0.9	darker, medium brown	darker than 3A	2
WA20-4	1.2	darker than 3A and 3C	darker than 4A; brownish black	2
WA20-5	1.5	similar to 4A	darker than 4C	2
WA20-6	1.8	reversal in downward darkening trend; medium brown	slightly darker than 6A	3
WA20-7	2.1	similar to 5A, but greyer, less brown	darker than 7A, greyer than 5C	4
WA20-8	2.4	similar to 7A	similar to 7C	4
WA20-9	2.7	greyer, less brown than -7 and -8	finer almost black	4
WA20-10	3.0	brown colour fading and grey-black increasing	similar to 9C	4

Summary

- Group 1: light medium-brown; aggregates (clumps) sparse and small
 Group 2: lacks the ochreous, limonitic tint of Group 1; progressively darker in samples 3 to 4 to 5; clumps common in Groups 2, 3, 4
 Group 3: reversal in that ochreous colour more intense and disrupts the progressive downward darkening trend
 Group 4: characteristically greyer, less brownish than the upper samples

*moderately magnetic fraction have colours intermediate to those of A and C.

Table 3. Microprobe analyses of atoll-texture pseudomorphs of pyrrhotite in sample WA20-9

wt. % Fe S	Grain 1		Grain 2		Grain 3		Grain 2		Grain 3	
	pyrrhotite, residual core	marcasite rim	marcasite rim	marcasite rim	marcasite rim	dark core	marcasite rim	dark core	marcasite rim	dark core
	60.4	43.1	43.0	43.0	43.0	33.4	43.0	33.4	43.0	33.6
	37.9	46.5	49.7	49.7	50.6	20.6	50.6	20.6	50.6	17.9
	<u>98.3</u>	<u>89.6</u>	<u>92.7</u>	<u>92.7</u>	<u>93.6</u>	<u>54.0</u>	<u>93.6</u>	<u>54.0</u>	<u>93.6</u>	<u>51.5</u>
Analyst: D.R. Owens										

Pyrrhotite and marcasite analyzed using "pyrrhotite 481" as a standard; sulphur values for the dark cores were obtained at the lower wavelength for S in a barite (BaSO₄) standard.

Table 4. General alteration trends in core WA-20

Sample numbers	Depth, metres	Alteration Features	Elemental S, wt. %
WA20-1, -2	0.3, 0.6	strong oxidation of sulphides; negligible pyrrhotite; goethite abundant, some jarosite	0.22 in WA20-1
WA20-3	0.9	numerous pyrrhotite remnants; strong alteration of pyrrhotite to goethite and native sulphur	1.63
WA20-4, -5, -6	1.2, 1.5, 1.8	pyrrhotite alteration less intense; marcasite rims start to appear at 1.8 m	2.54 in WA20-6
WA20-7, -8	2.1, 2.4	weaker alteration of pyrrhotite -- some rims incomplete, but marcasite content higher	
WA20-9, -10	2.7, 3.0	many pyrrhotite edges unaltered; homogeneity of marcasite reaches its peak in WA20-9	0.23 in WA20-10

Table 5. Chemical analyses of soluble sulphate in core WA20

Sample number	Depth, metres	Sample weight	Soluble SO_4 , wt. %
WA20-2	0.6	2.9083 g	2.41
WA20-4	1.2	2.9971	1.45
WA20-6	1.8	2.9941	2.50
WA20-8	2.4	3.0433	2.30
WA20-10	3.0	2.9840	1.50

Samples slurried in 300 mL H_2O at room temperature for 30 minutes; solution filtered and a few drops HCl added to prevent Fe precipitation; SO_4 analyzed by ion chromatography. Analyst: D.J. Hardy.

